

Monitoring / Verification using DMS: TATP Example

Manuel Manard, Department of Homeland Security (Postdoctoral Fellow assigned to Special Technologies Laboratory), 805-681-2121; manardmj@nv.doe.gov; Stephan Weeks (Senior Scientist) and Kevin Kyle (Principal Scientist), U.S. Department of Energy, Special Technologies Laboratory (Operated by National Security Technologies, LLC), 5520 Ekwill Street, Suite B, Santa Barbara, CA 93111; 805-681-2262, weeeekssj@nv.doe.gov; 805-681-2283, kylekr@nv.doe.gov.

Abstract—Field-rugged and field-programmable differential mobility spectrometry (DMS) networks provide highly selective, universal monitoring of vapors and aerosols at detectable levels from persons or areas involved with illicit chemical/biological/explosives (CBE) production. CBE sensor nodes used in conjunction with automated fast gas chromatography with DMS detection (GC/DMS) verification instrumentation integrated into situational operations-management systems can be readily deployed and optimized for changing application scenarios. The feasibility of developing selective DMS nodes for a “smart dust” sampling approach with guided, highly selective, fast GC/DMS verification analysis is a compelling approach to minimize or prevent the illegal use of explosives or chemical and biological materials.

DMS is currently one of the foremost emerging technologies for field separation and detection of gas-phase chemical species. This is due to trace-level detection limits, high selectivity, and small size. Fast GC is the leading field analytical method for gas phase separation of chemical species in complex mixtures. Low-thermal-mass GC columns have led to compact, low-power field systems capable of complete analyses in 15–300 seconds. A collaborative effort optimized a handheld, fast GC/DMS, equipped with a non-rad ionization source, for peroxide-based explosive measurements.

Index Terms—Chemical analysis, Differential Mobility Spectrometry, Real-time systems, Sensor nodes

I. INTRODUCTION

A handheld, direct air sampling, highly selective, dual-technology, trace-level (~ppb) chemical, biological, and explosives (CBE) detector has been developed. Initially the detector was optimized to detect peroxide-based explosives using a nonradiological ionization source. Triacetone triperoxide (TATP) was the primary target analyte, largely due to its implicated usage in the Shoe Bomber and Heathrow Airport events that led to implementation of shoe removal and the 3-1-1 rule for carry-on liquids at airport security portals. Project success led to a novel monitoring / verification concept for a handheld system operations protocol applicable to various remote monitoring and sensing scenarios.

Initial chemical vapor detection is performed using small, low-power sensor nodes followed by verification and chemical

identification using a robotic or handheld chemical analysis unit. For example, a field asymmetric ion mobility spectrometry (FAIMS) MEMS sensor continuously and selectively monitors air in the environment; an above-threshold response triggers a smart-sampling system for preconcentration, dilution and dual-technology verification analysis (i.e., a fast gas chromatography (fGC)/FAIMS system). The FAIMS trigger signal aids the identification of the application- or scenario-specific analysis method to be used for verification, which can typically be performed in 15–200 seconds using the fGC/FAIMS detection system. The fGC provides matrix simplification and, therefore, extremely high selectivity analyte (e.g., TATP) verification in combination with the FAIMS detector. Additionally, results show the feasibility of developing the FAIMS sensor as a field-programmable node for distributed mesh wireless sensor network (WSN) applications allowing for wide-area CBE sampling, which could guide a robotically controlled fGC/FAIMS system to give verification analysis. These various remote sensing and monitoring schemes are compelling approaches to minimize or prevent the use of explosives, or CBE agents, in illegal activities. Implementation of such an approach could shift the fear-factor from the public arena to the perpetrators and their organizations.

Terrorism in the global community often involves the use of improvised explosive devices (IEDs) that directly endanger lives, provide distractions from other activities, or instigate panic. Many IEDs can be manufactured from materials commonly found in households and hardware stores. Two peroxide-based liquid explosives, TATP and hexamethylene triperoxide diamine (HMTD), are synthesized from common chemicals such as hydrogen peroxide, acetone, sulfuric acid, ammonia, and citric acid (Figure 1). Recipes can be readily found on the internet by anyone seeking to generate sufficient quantities of these highly explosive chemicals to cause considerable collateral damage. Detection of TATP and HMTD by advanced sensing systems can provide the early warning necessary to prevent terror plots from coming to fruition.

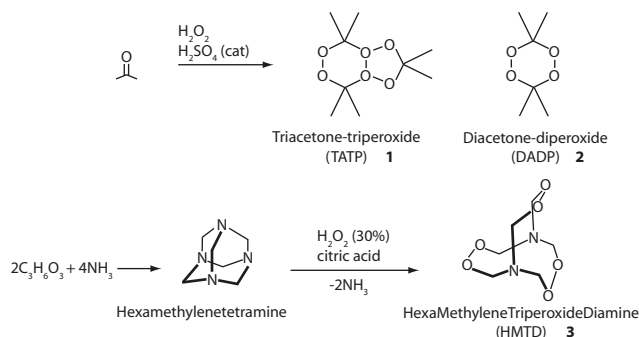


Figure 1 - Synthesis scheme for TATP and HMTD

Developing CBE sensors that provide easily interpreted information in real-time is currently at the forefront of many research and development (R&D) efforts. Complicated sampling and user interfaces or extensive analysis times could lead to increased response times for first responders in situations where minutes could mean the difference between life and death. Technologically advanced, networked CBE sensor systems with intelligent data analysis would facilitate making rapid decisions regarding how to respond in an emergency situation. National security and disaster response teams need field portable CBE sensor systems. These systems must be capable of plug-and-play integration of advanced sensor technologies and be amenable to rapid applications development for ever-changing scenarios. CBE sensor system platforms of this nature will allow the U.S. to maintain its technological advantage in combating terrorism.

II. SYSTEM INTEGRATION

A. Design Concept

FAIMS, also known as differential mobility spectrometry (DMS), is currently one of the foremost emerging technologies for field separation and detection of gas-phase chemical agents. This is primarily attributable to its small size, trace-level detection limits, and its ability to identify a substance by inspection of the ion mobility spectrum. This method separates and identifies ions at ambient pressures by utilizing the non-linear dependence of an ion's mobility on the radio frequency (rf) electric field strength. Incoming vapor molecules are ionized in an ionization chamber. Once ions exit the ionization chamber, they are carried by a gas stream to the analytical region. Here, ions are subjected to an asymmetric alternating rf electric field (V_{rf}). The mobility of an ion in high electric fields ($E > 10,000 \text{ V/cm}^2$) is dependent on the electric field; thus, alternating between high and low fields changes the ion mobility. This gives rise to unstable trajectories for some ionic species, causing them to collide with the walls of the analyzer region. An additional dc compensation voltage (V_c) is also superimposed on the rf field, serving to modify ion trajectories and allowing them to be directed onto detector elements. The FAIMS spectrum is recorded by measuring the ion intensity as a function of both the rf and dc electric fields. The ion mobility dependence on the electric field is given by equation 1 [1]:

$$K(E/N) = K(0) + (1 + \sum_{k=1}^N \alpha_{2k} (E/N)^{2k}), \quad (1)$$

where $K(0)$ is the mobility of an analyte in the low field limit, E/N is the ratio between the electric field and the gas density, and α_{2k} are analyte-dependent coefficients.

GC is a leading analytical method for the separation of gas phase chemical species in complex mixtures. Advances in the technique have led to the development of low thermal mass (LTM) fast GC columns. These columns are capable of completing separation runs in less than 3 minutes. These fast GC columns are also more compact and require lower power for operation than their traditional counterparts.

STL worked with Sionex Corp. under a one-way nondisclosure agreement and their early technology access program to acquire the DMS detector evaluation platform (SVAC) and to

develop a fGC/DMS MicroAnalyzer™ system equipped with a photoionization source (Kr lamp, 10.6 eV) and optimized for the detection of TATP. The schematic shown in Figure 2 illustrates the original operations concept for the prototype handheld unit. The fGC/FAIMS unit is the heart of the system. However, to lengthen service time and minimize maintenance, we add a FAIMS detector for continuous monitoring. When the continuous monitor alerts the system that there is something that merits further investigation, a “smart sampling” interface is engaged. Smart sampling controls sample introduction so target analytes remain in the calibrated portion of the analytical response curves of the fGC/FAIMS. Smart sampling permits analyte preconcentration (e.g., solid phase microextraction [SPME]) or dilution as needed. The sample is then sent to the fGC/FAIMS detector for verification. A desorption sampler for surfaces and particles can also be configured.

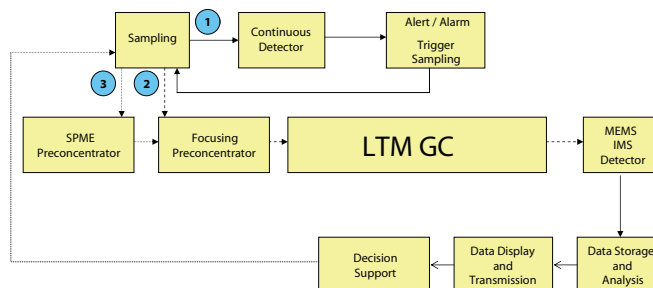


Figure 2 - Schematic of the prototype handheld peroxide explosives detector system

B. Continuous Direct Air Sampling FAIMS Monitoring

A direct air sampling system was designed and developed for the DMS evaluation platform (SVAC) to facilitate its use as a continuous monitoring system. A micro-diaphragm pump (KNF Neuberger, Inc) was used to pull in gas-phase analytes directly from the environment for separation and detection with the DMS system (Figure 3). The combined SVAC and air-sampling unit measures $9.8" \times 4.6" \times 3.2"$, weighs 3.1 lbs, and utilizes a ^{63}Ni source to ionize incoming compounds. A re-circulating air transport gas (vs sampled gas) system for the SVAC unit was incorporated to eliminate the need for cumbersome gas cylinders, thus further simplifying use and maintenance requirements of the instrument.

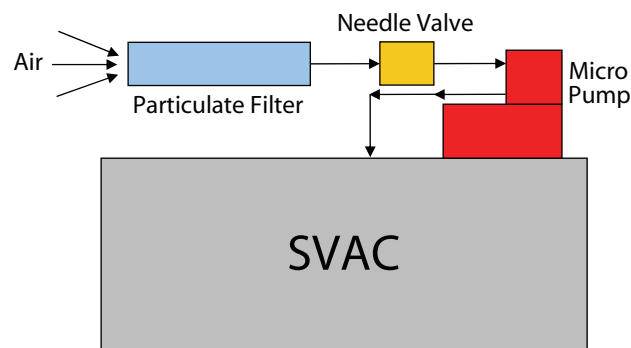


Figure 3 - Schematic of FAIMS unit with air sampling system

Analytes entering the DMS unit are separated and identified by their characteristic response to the compensation voltage at a given V_{rf} (Table 1). This response was observed to be unique for a wide range of substances studied in our laboratory relative to the residual ion peaks (RIPs) from the continuous-feed air sampler. RIPs result from air ionization by the ^{63}Ni source (β^- , 17.4 keV).

Table 1 - Summary of Results for Continuous Sampling of Gas-Phase Compounds^a

Chemical	Compensation Voltage (V_c) ^b	
	Positive Ions	Negative Ions
$\text{C}_2\text{H}_2\text{F}_4$	-24.1	-20.2
NH_3	-12.5 -10.0	-16.5 (weak)
SF_6	-	-4.9
C_2HCl_3	-	-17.8
$\text{C}_2\text{H}_4\text{F}_2$	-31.3	-26.0
MEK	-3.8	-
Acetone	-5.0 -1.4	-
Methanol	-14.3 -7.3	-3.3 (weak)
Ethanol	-8.4	-4.3
Residual Ion Peaks	-17.2 -15.5	-14.9

^a $V_{rf} = 900 \text{ V}$
^b Two numbers in a single cell indicate two peaks are characteristic for the species

Figures 4 and 5 show the characteristic responses of SF_6 and ethanol, respectively. For SF_6 , only the negative ion spectrum is shown because no positive ion response is observed. This illustrates an additional detection capability of FAIMS. The identity of an analyte can be determined based on whether it gives a positive, negative, or combined signal in addition to its V_c dependence, furthering the specificity of the technique.

A critical parameter to the proper functionality of the instrument has been determined to be the flow rate of the sampled air into the system. Flow rates of 8–12 ml/min have been found to yield results that are highly reproducible with good signal-to-noise ratios (for examples, see Figures 4 and 5). Increasing the flow rate of the sampling system can lead to excessively noisy spectra and erratic peak positions for both RIPs and analytes. Some of this behavior is attributable to pulsations in the sampling flow that occur at higher flow rates. Restricting the flow to relatively low rates effectively eliminates these pulsations.

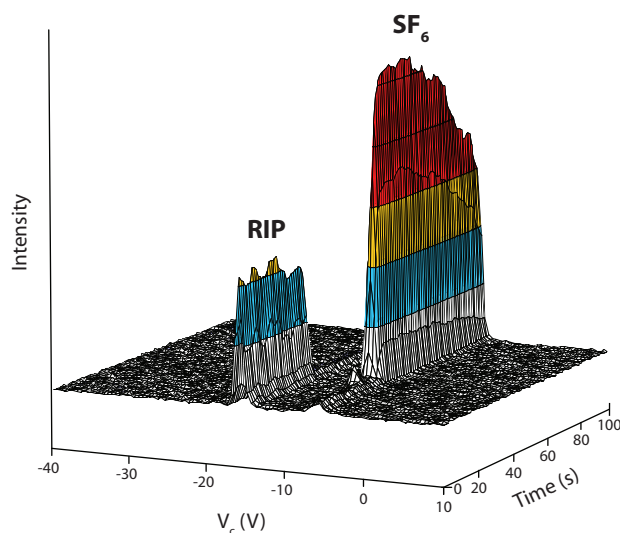


Figure 4 - Negative ion FAIMS spectrum of SF_6

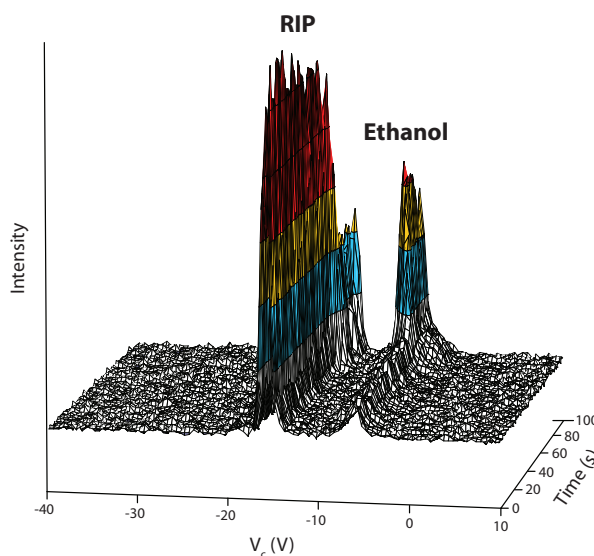
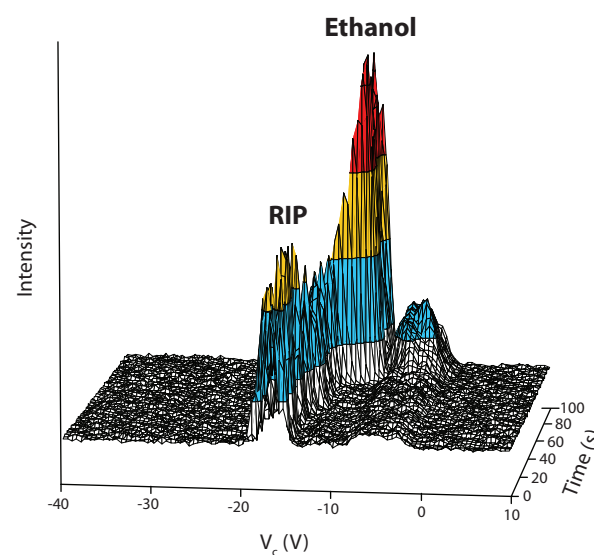


Figure 5 - Positive (top) and negative (bottom) ion FAIMS spectra of ethanol

Initially, a time interval of approximately 20 seconds was observed from the introduction of the sample to the appearance of the analyte peak in the FAIMS spectrum. This was attributed to the relatively low sampling flow rates required by the instrument. Recovery times of the system varied from nearly instantaneous to several minutes, depending on the concentration of the analyte in the sampled air. The system is designed to be a trace-level detector. Thus, if analyte concentrations are in the appropriate range (ppt–ppm), then recovery times are nearly instant. The smart sampling system has been designed to compensate for the concentration dependence of the recovery time, providing more rapid (~1 second) response times using “concentration/dilution logic” to handle the wide variation of target concentrations expected in the field.

C. fGC/FAIMS Target Analyte Verification Analysis

In the field, the target explosive chemical of interest is often present in varying and complex matrices. A high degree of selectivity, or specificity, may be required to obtain decision-quality data or information. In order to enhance the confidence in the measurement, our R&D efforts developed the rapid sampling and verification analysis portion of the system for situations or environments where the FAIMS continuous monitoring data alone may not be enough to produce conclusive evidence to identify the target analyte. Furthermore, the project specifically targeted optimization of the handheld unit for the detection of TATP. Over the past 2–3 years, prior R&D efforts to develop fieldable fast GC systems and methods similar to this current project have prompted us to work with Sionex to develop a FAIMS detector for the fast GC. The Sionex unit was equipped with a (non-radioactive) photoionization source and had components and suitable methods that were optimized for the detection of TATP. The Sionex efforts included using air as the GC carrier gas, and developing a recirculating transport gas cleanup system for GC and FAIMS operation and a sampling adsorbent cell for flash-heating sample introduction onto the GC column. Their fGC/FAIMS unit combines the separation capabilities of GC with the selectivity of FAIMS. It measures 9.5" × 5.25" × 3.5" and weighs 3.8 lbs. Experimentation demonstrated the unit has been optimized for the detection of the peroxide explosives, TATP and HMTD (Figure 6). Analysis times required to obtain results for these analytes are approximately 80 seconds for TATP and 160 seconds for HMTD (Figure 7). Analytes are identified both by their elution time from the column and by their characteristic response in the DMS spectrum.

The fGC/FAIMS response to substances that could interfere with the detection of peroxide-based explosives has been studied. Both the GC elution time and the DMS spectral peaks were unique and well resolved, and do not hinder the detection of either TATP or HMTD. Limits of detection were determined for TATP and HMTD by systematically varying the concentrations of the peroxides in acetonitrile solution and integrating over the peak areas observed in the chromatograms (Figure 7). These values were plotted versus concentration to generate calibration curves for the instrument (Figure 8). The limit of detection for both TATP and HMTD is approximately 1 ng/μL for the current method. The calibration curves also show that the linear dynamic range of the unit is greater than two orders of magnitude for the detection of these analytes. Results were verified by GC / mass spectrometry (GC/MS).

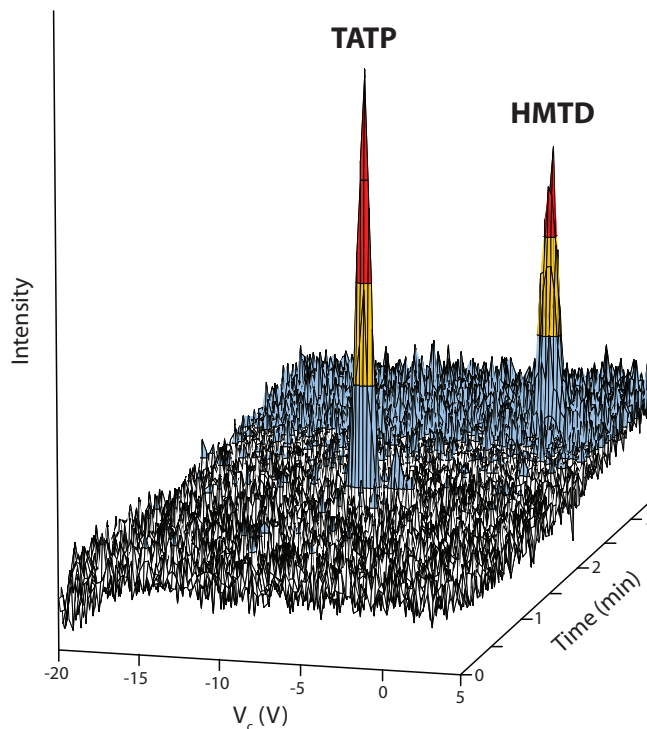


Figure 6 - GC/DMS spectrum of TATP and HMTD

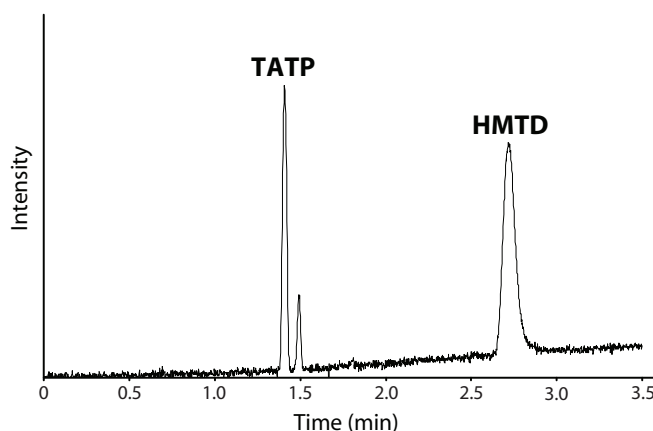


Figure 7 - Fast gas chromatograms of TATP and HMTD

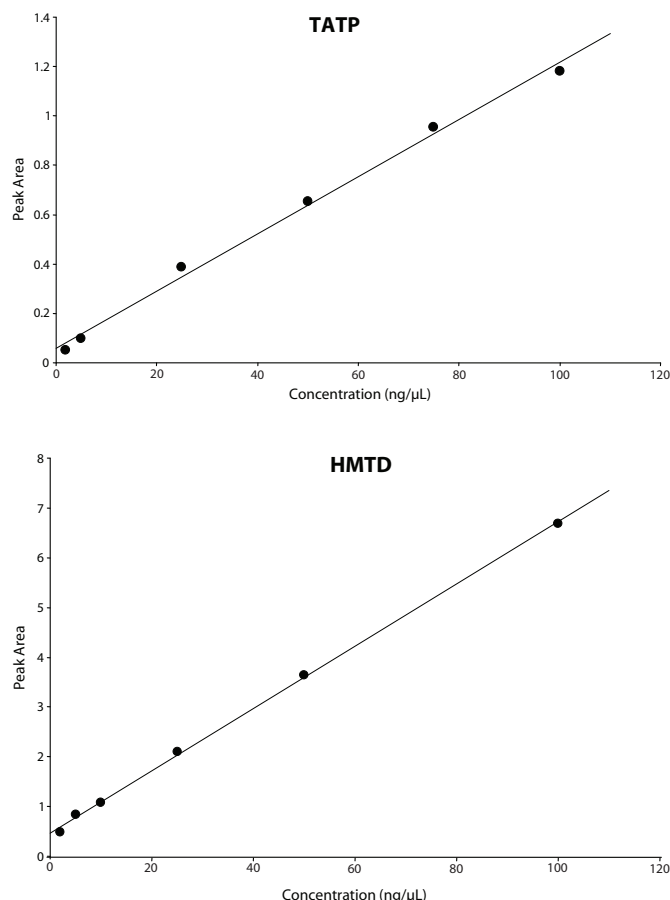


Figure 8 - Calibration curves for TATP and HMTD, respectively. Limits of detection for both analytes were determined to be less than 1 ng/μL.

III. CONCLUSION

We have successfully demonstrated the specificity and sensitivity of the FAIMS technology, and its ability to continuously sample directly from the environment and provide real-time chemical signature data to detect and identify our target analytes, TATP and HMTD. Both the continuous sampling FAIMS device and the fGC/FAIMS sensor are ready to be integrated into STL's situational operations management software and combined into a single, handheld system with GPS, providing selective detection of a host of substances, including other explosives (e.g., TNT, RDX), TICs/TIMs, CWAs and other agents. The FAIMS units are capable of being programmed remotely for field operations. Future research directions include reduction of the overall size of the unit and the development of protocol for intelligent data analysis and operations. Alternative non-radiological ionization sources are also under investigation to address the issue of transport of a radioactive source, and the limitations on the list of detectable chemicals with the lamp source.

The FAIMS detector is a MEMS device, which can be developed into a CBE sensor mote for distributed mesh WSN applications. A "Smart Dust" concept with FAIMS sensor motes for selective and widespread sampling, followed

by highly selective fast GC/FAIMS for verification analysis, can be envisioned for wide-area protection against the use of CBE agents.

This innovative dual-technology approach using fast and selective separation plus selective ion detection minimizes or eliminates false signals. The innovative continuous monitoring plus rapid verification analysis approach provides rapid alert (within seconds) with enhanced measurement confidence in less than 2–3 minutes, and also lengthens in-field service of the detector system. The small prototype size (~4" × 3" × 9") may be further reduced by systems design engineering. Further development of smart sampling of trace (ppt to ppm) vapor and rapid integration into systems operations management software will lead to automated, fully programmable CBE detection for field operations, providing the capability to respond to changing deployment and sampling scenarios with application-specific analysis methods. Expert feedback and rapid methods development could be accomplished remotely and globally.

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REFERENCES

- [1] Eiceman, G. A., Z. Karpas, Ion Mobility Spectrometry, Boca Raton: CRC Press, 2005.